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by

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Coordinates which Diagonalize the Kinetic Energy of Relative Motion*

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ABSTRACT

The most general sets of coordinates which diagonalize the relative kinetic energy of an N particle system are derived. These include reaction coordinates which are symmetric with respect to both the reactants and products. The angle of skewing of an idealized potential energy surface determines whether a molecular collision is adiabatic or leads to an exchange reaction. The shape of the potential energy surface leads to vibrationally excited diatomic molecules as products in hydrogen-halogen reactions.

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I owe a great debt of gratitude to Henry Eyring for having given me a good start in my scientific career. His physical insight and his ability to construct simple models for explaining natural phenomena was a great inspiration. The present research is an outgrowth of my graduate work with him.

The objective of this paper is to derive the most general sets of coordinates which diagonalize the relative kinetic energy of an N particle system. Such coordinates are useful in both stationary states and collision processes. In a subsequent paper some of the quantum mechanical applications will be considered: isotopic shifts of the energy, deviations from the Born-Oppenheimer separation, spin and orbital angular momentum couplings, etc. The present paper is written from the standpoint of molecular collisions or chemical kinetics. For example, our coordinates might be used in the construction of potential energy surfaces.

The concept of potential energy surfaces is an example of the genius of both Henry Eyring and Michael Polanyi.¹ In 1930, they knew from quantum mechanics how to estimate the potential energy of an arbitrary configuration of atoms. They asked the question, how could they construct an energy surface, expressed in terms of the relative separation between atoms, such that force on a hypothetical marble rolling on this surface is equal to minus the gradient of the energy and the motion of the marble faithfully reproduces the kinematics of a molecular collision process. They consulted with their good friend, Eugene Wigner. The energy contours should correspond to the effective potential energy, V_{eff} , which is the sum of the potential energy, V (the Born-Oppenheimer

approximation to the electronic energy of the molecular array), and the centrifugal potential $\mathcal{L}^2/2I$, where \mathcal{L} is the total angular momentum of the system (a constant of the motion) and I is the moment of inertia,

$$V_{\text{eff}} = V + (\mathcal{L}^2/2I) \quad (1)$$

Furthermore, the coordinates should be linear combinations of the separations between the atoms, chosen so as to diagonalize the kinetic energy of the relative motion. Thus, when I was a graduate student, Eyring's office was filled with both cardboard and plaster of paris potential energy surfaces to simulate head-on collisions of atoms with diatomic molecules -- and one of our functions was to roll the marbles!

I. COORDINATE SYSTEMS WHICH DIAGONALIZE THE KINETIC ENERGY OF RELATIVE MOTION

In treating the kinematics of a many-body problem by either classical or quantum mechanics, it is desirable to shift from space-fixed coordinates to relative coordinates and separate off the motion of the center of mass. The resulting expressions for the kinetic energy usually contain cross-terms in the relative velocities or momenta. The presence of these cross-terms greatly complicates the dynamics. It was the presence of such cross-terms which led Eyring and Polanyi¹ to skew the relative coordinates in treating the interaction of three hydrogen atoms. Their skewed coordinates represent a new set of relative coordinates, which is indeed a special case of the general coordinates (without such cross-terms) which we shall consider here.

There are a great many different sets of relative coordinates which yield an expression for the kinetic energy of relative motion

in diagonal form. Some of these sets have been considered previously by Jepsen and Hirschfelder² and by Hirschfelder and Dahler.³ They found that the kinetic energy of an N-particle system has the form

$$T = \frac{1}{2} [\dot{Q}_1^2 + \dot{Q}_2^2 + \dots + \dot{Q}_N^2] \quad (2)$$

Their sets of coordinates, Q_i , can be visualized in terms of "mobile" models.

The mobile is constructed in the following manner: The coordinate Q_N is a vector joining the center of mass of the system to the origin of the laboratory coordinates,

$$Q_N = M_N^{-\frac{1}{2}} \sum_{j=1}^N m_j \underline{r}_j \quad (3)$$

Here \underline{r}_j is the position and m_j is the mass of the j-th particle; M_N is the mass of the system, $M_N = \sum_{j=1}^N m_j$. Throughout the rest of this paper, the definition of Q_N remains unchanged whereas there is considerable choice in the selection of the N-1 relative coordinates.

The other (N-1) coordinates are vectors joining together the centers of gravity of groups of particles. Let $\underline{r}_c(A)$ be the center of mass and M_A be the mass of the particles in group A,

$$M_A = \sum_{\alpha \in A} m_\alpha, \quad \underline{r}_c(A) = \sum_{\alpha \in A} m_\alpha \underline{r}_\alpha / M_A \quad (4)$$

Then the coordinate joining group A with group B is

$$Q_i = (M_A M_B / (M_A + M_B))^{\frac{1}{2}} [\underline{r}_c(A) - \underline{r}_c(B)] \quad (5)$$

If a group A consists of a single particle, M_A is the mass and

$\underline{r}_c(A)$ is the coordinate of that particle. To (or from) each particle there is exactly one vector coordinate. Any mobile constructed in the above manner will furnish a suitable set of coordinates Q_1, \dots, Q_N which satisfies Eq. (2). For two particles (such as the hydrogen nucleus and electron), Q_1 is the square root of the reduced mass times the separation between particles. Fig. 1 shows the three possible mobiles for a three particle system. Fig. 2 shows three of the many possible mobiles for 4 particles.

All of the possible sets of coordinates Q'_1, \dots, Q'_{N-1} which (together with Q_N) satisfy Eq. (2) can be generated by unitary transformations (rotations and reflections in a space of $N-1$ dimensions) of any set of coordinates Q_1, \dots, Q_{N-1} (which might, for example, be obtained from a mobile) In order to prove this, let

$$Q'_i = \sum_{j=1}^{N-1} R_{ij} Q_j, \quad i = 1, \dots, N-1 \quad (6)$$

Then,

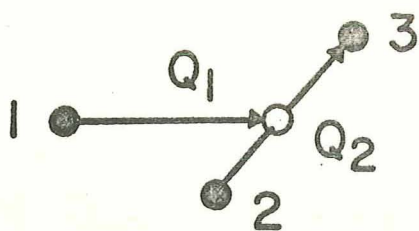
$$\sum_{i=1}^{N-1} Q'^2_i = \sum_{i=1}^{N-1} \sum_{j=1}^{N-1} \sum_{k=1}^{N-1} R_{ij} R_{ik} Q_j Q_k \quad (7)$$

If, now, the coefficients R_{ij} form a unitary matrix so that

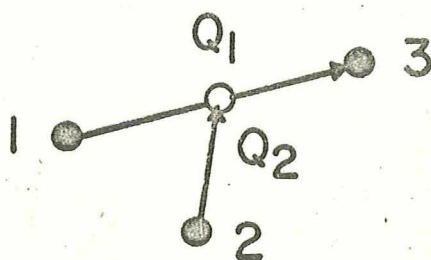
$$\sum_{i=1}^{N-1} R_{ij} R_{ik} = \delta_{jk} \quad (8)$$

then

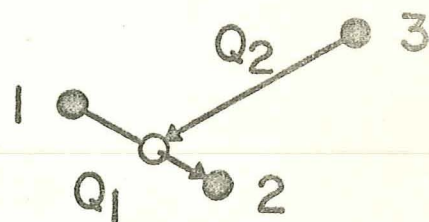
$$\sum_{i=1}^{N-1} Q'^2_i = \sum_{j=1}^{N-1} Q^2_j \quad (9)$$



(a)



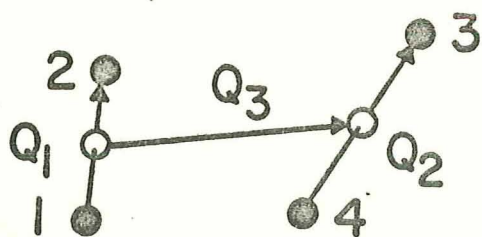
(b)



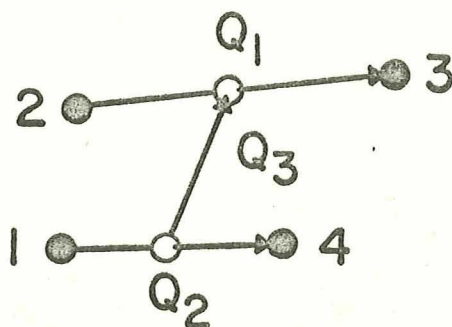
(c)

Fig. 1: The Three Possible Mobiles for a Three Particle System.

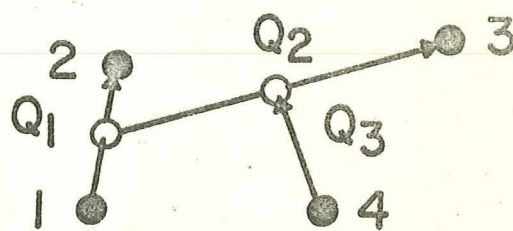
The solid circles are particles, whereas the open circles are centers of mass of groups of particles. If particle "1" reacts with molecule "23", the initial phase of the reaction is best described by Mobile (a). If the products of the reaction are "2" + "13" or "3" + "12" the completion of the reactive collision is best described by Mobile (b) or (c) respectively.



(a)



(b)



(c)

Fig 2: Three of the Many Possible Mobiles for a Four Particle System.

For, If molecule "12" collides with molecule "34", Mobile (a) is a good description. Mobile (b) describes the reaction products "23" and "14". Mobile (c) is one of many alternate descriptions.

Thus any unitary transformation applied to an acceptable set of coordinates Q_1, \dots, Q_{N-1} produces another acceptable set of coordinates Q'_1, \dots, Q'_{N-1} . Since Eq. (8) places $N(N-1)/2$ restrictions on the $(N-1)^2$ coefficients R_{ij} , there are

$$(N-1)^2 - \frac{N(N-1)}{2} = \frac{(N-1)(N-2)}{2}$$

arbitrary parameters embedded in the R_{ij} matrix. On the other hand, let us consider the most general expression for the relative coordinates Q'_1, \dots, Q'_{N-1} ,

$$Q'_i = \sum_{j=1}^{N-1} A_{ij} (r_j - r_N), \quad i = 1, \dots, N-1 \quad (10)$$

There are altogether $(N-1)^2$ coefficients A_{ij} . Eq. (2) imposes $N(N-1)/2$ conditions on the A_{ij} , since of these $(N-1)(N-2)/2$ correspond to the vanishing of the cross-terms and $(N-1)$ conditions correspond to the requirements for the diagonal terms in the relative kinetic energy. Thus, the number of arbitrary parameters in the A_{ij} is just exactly equal to the number of arbitrary parameters embedded in the R_{ij} . We conclude that every acceptable coordinate set can be generated from one set by a suitable unitary transformation.

A. Three Particle Coordinates

In order to understand the significance of the various coordinate systems, let us consider the three particle system in great detail.

Corresponding to mobile (a) of Fig. 1, there are two relative coordinates

$$Q_1 = \left[\frac{m_1(m_2 + m_3)}{M} \right]^{\frac{1}{2}} \left[-r_1 + \frac{m_3 r_3 + m_2 r_2}{m_2 + m_3} \right] \quad (11)$$

and

$$Q_2 = \left[\frac{m_2 m_3}{m_2 + m_3} \right]^{\frac{1}{2}} [r_3 - r_2] \quad (12)$$

These can be expressed in the form

$$Q_1 = \alpha (r_2 - r_1) + \beta (r_3 - r_2) \cos \phi \quad (13)$$

and

$$Q_2 = \beta (r_3 - r_2) \sin \phi \quad (14)$$

Here

$$\alpha = [m_1(m_2 + m_3)/M]^{\frac{1}{2}}, \quad \beta = [m_3(m_1 + m_2)/M]^{\frac{1}{2}} \quad (15)$$

and

$$\cos \phi = \left[\frac{m_1 m_3}{(m_1 + m_2)(m_2 + m_3)} \right]^{\frac{1}{2}} \quad (16)$$

As Fig. 3 shows, Q_1 and Q_2 correspond to Eyring and Polanyi's¹ famous "skewed coordinates". Table 1 shows how ϕ , α , and β depend upon the relative masses. When the three masses are equal, $\phi = 60^\circ$ and $\alpha = \beta = (2m_2/3)^{\frac{1}{2}}$.

In accordance with our theorem any acceptable coordinates, Q_1' and Q_2' , are determined (except for their sign) by a rotation of the coordinates Q_1 and Q_2 through an angle θ ,

$$Q_1' = Q_1 \cos \theta + Q_2 \sin \theta \quad (17)$$

Fig. 3: The Eyring-Polanyi "Skewed" Coordinates.

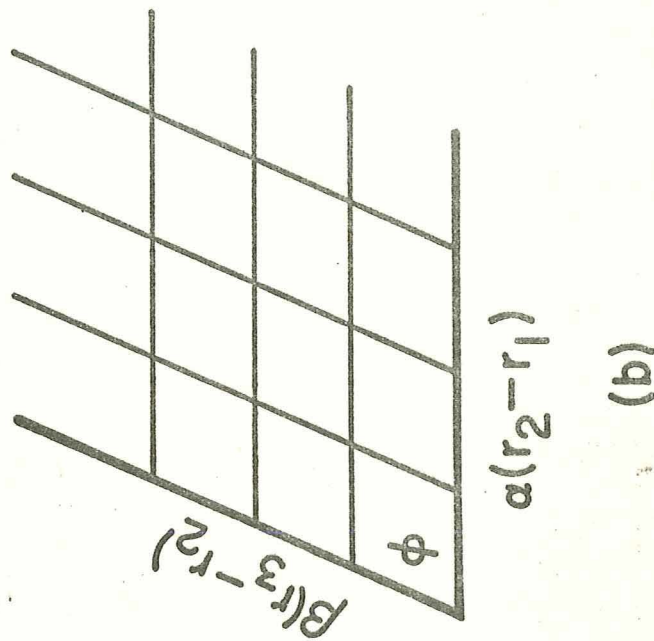
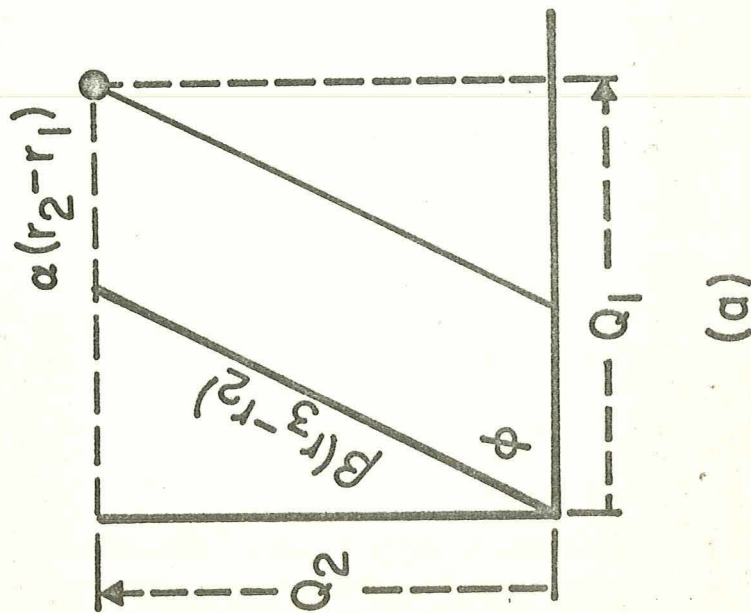


Fig. 3a shows the relationship between the relative coordinates $\alpha(r_2 - r_1)$ and $B(r_3 - r_2)$ and the Q_1 and Q_2 . As indicated in Fig. 3b, potential energy surfaces are usually constructed with respect to $\alpha(r_2 - r_1)$ and $B(r_3 - r_2)$. Therefore the coordinates appear to be skewed. Since the relative coordinates are vectors, this figure corresponds to three figures in terms of scalar projections.

Table 1: Three Particle Coordinate Parameters

m_1/m_2	m_3/m_2	ϑ	$\alpha/m_2^{\frac{1}{2}}$	$\beta/m_2^{\frac{1}{2}}$
3	3	$41^{\circ} 25'$	1.30931	1.30931
3	2	45°	1.22474	1.15470
3	1	$52^{\circ} 14'$	1.09545	0.89443
3	1/2	60°	1.00000	0.66667
3	1/3	$64^{\circ} 20'$	0.96077	0.55470
2	2	$48^{\circ} 11'$	1.09545	1.09545
2	1	$54^{\circ} 44'$	1.00000	0.86603
2	1/2	$61^{\circ} 52'$	0.92582	0.65465
2	1/3	$65^{\circ} 54'$	0.89443	0.54772
3/2	3/2	$53^{\circ} 8'$	0.96825	0.96825
3/2	1	$56^{\circ} 47'$	0.92585	0.84517
3/2	1/2	$63^{\circ} 26'$	0.86597	0.64550
1	1	60°	0.81650	0.81650
1	1/2	$65^{\circ} 54'$	0.77460	0.63246
1	1/3	$69^{\circ} 18'$	0.75593	0.53452
1/2	1/2	$70^{\circ} 32'$	0.61237	0.61237
1/2	1/3	$73^{\circ} 13'$	0.60302	0.52223
1/3	1/3	$75^{\circ} 31'$	0.51640	0.51640

and

$$Q_2' = -Q_1 \sin \theta + Q_2 \cos \theta \quad (18)$$

Thus, if $\theta = \emptyset - \pi/2$ so that $\cos \theta = \sin \emptyset$ and $\sin \theta = -\cos \emptyset$,

$$Q_1' = \left[\frac{m_1 m_2}{m_1 + m_2} \right]^{\frac{1}{2}} [r_2 - r_1] \quad (19)$$

and

$$Q_2' = - \left[\frac{m_3 (m_1 + m_2)}{M} \right]^{\frac{1}{2}} \left[-r_3 + \frac{m_1 r_1 + m_2 r_2}{m_1 + m_2} \right] \quad (20)$$

The Q_1' and Q_2' of Eqs. (19) and (20) correspond to mobile (c) of Fig. 1. They can also be written in the form

$$Q_1' = \alpha (r_2 - r_1) \sin \emptyset \quad (21)$$

and

$$Q_2' = \beta (r_3 - r_2) + \alpha (r_2 - r_1) \cos \emptyset \quad (22)$$

Perhaps the most interesting coordinates are obtained by taking $\theta = (\emptyset/2) - (\pi/4)$. Using Eqs. (17) and (18) together with Eqs. (13) and (14) and Eqs. (21) and (22),

$$Q_1'' = 2^{-1} (1 - \cos \emptyset)^{-\frac{1}{2}} \begin{bmatrix} (1 + \sin \emptyset - \cos \emptyset) \alpha (r_2 - r_1) \\ -(1 - \sin \emptyset - \cos \emptyset) \beta (r_3 - r_2) \end{bmatrix} \quad (23)$$

and

$$Q_2'' = 2^{-1} (1 - \cos \emptyset)^{-\frac{1}{2}} \begin{bmatrix} (1 + \sin \emptyset - \cos \emptyset) \beta (r_3 - r_2) \\ -(1 - \sin \emptyset - \cos \emptyset) \alpha (r_2 - r_1) \end{bmatrix} \quad (24)$$

For a chemical reaction in which particle "1" collides with "23" to form "12" plus "3", the coordinates Q_1'' and $-Q_2''$ are symmetric with

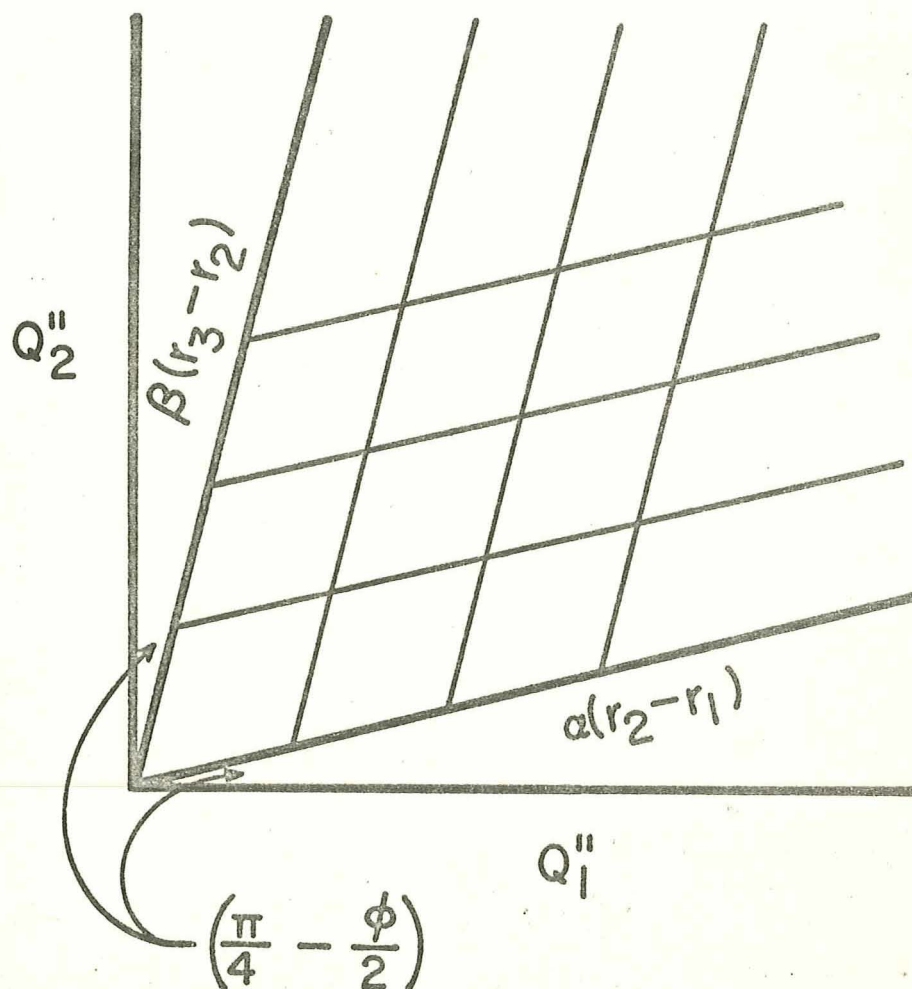


Fig. 4: Relationship Between the Coordinates Q_1'' and Q_2'' and the Potential Energy Surface.

As this figure shows, the potential energy surface as a whole has been rotated through the angle $(\pi/4) - (\phi/2)$. This establishes the basic symmetry of Q_1'' and Q_2'' with respect to $\alpha(r_2 - r_1)$ and $B(r_3 - r_2)$. Since the relative coordinates are vectors, this figure corresponds to three figures in terms of scalar projections.

$$Q_1 = \alpha (r_2 - r_1) \sin \phi \quad (30)$$

$$Q_2 = \gamma (r_4 - r_3) \sin \theta \quad (31)$$

$$Q_3 = \alpha (r_2 - r_1) \cos \phi + \beta (r_3 - r_2) + \gamma (r_4 - r_3) \cos \theta \quad (32)$$

where

$$\cos \phi = \left[\frac{m_1(m_3 + m_4)}{(m_1 + m_2)(M - m_1)} \right]^{\frac{1}{2}} \quad (33)$$

$$\cos \theta = \left[\frac{m_4(m_1 + m_2)}{(m_3 + m_4)(M - m_4)} \right]^{\frac{1}{2}} \quad (34)$$

and

$$\alpha = [m_1(M - m_1)/M]^{\frac{1}{2}} \quad (35)$$

$$\beta = [(m_1 + m_2)(m_3 + m_4)/M]^{\frac{1}{2}} \quad (36)$$

$$\gamma = [m_4(M - m_4)/M]^{\frac{1}{2}} \quad (37)$$

From Eqs. (30) - (32) it follows that in the $Q_1 Q_2 Q_3$ space, the relative coordinates $\alpha(r_2 - r_1)$, $\beta(r_3 - r_2)$, $\gamma(r_4 - r_3)$ are skewed. Thus, the four particle potential energy surfaces expressed in terms of $\alpha(r_2 - r_1)$, $\beta(r_3 - r_2)$, $\gamma(r_4 - r_3)$ have coordinate grids which are skewed parallelepipeds. If the masses are equal, $\phi = \theta = 54^\circ 44'$ and $\alpha = \gamma = (3m_1/4)^{\frac{1}{2}}$ and $\beta = m_1^{\frac{1}{2}}$.

The coordinates $-Q'_3$, $-Q'_1$, and Q'_2 corresponding to mobile (b) of Fig. 2 can be expressed in terms of Q_1 , Q_2 , and Q_3 by means of Eq. (6) where the unitary matrix \underline{R} is given by (for convenience, let $m_{ij} = m_i + m_j$),

$$\underline{R} = \begin{pmatrix} \left(\frac{m_1 m_2 M}{m_{12} m_{14} m_{23}} \right)^{\frac{1}{2}} & - \left(\frac{m_3 m_4 M}{m_{12} m_{23} m_{34}} \right)^{\frac{1}{2}} & \left(\frac{m_1 m_3 - m_2 m_4}{m_{12} m_{14} m_{23} m_{34}} \right)^{\frac{1}{2}} \\ \left(\frac{m_1 m_3}{m_{12} m_{23}} \right)^{\frac{1}{2}} & \left(\frac{m_2 m_4}{m_{23} m_{34}} \right)^{\frac{1}{2}} & - \left(\frac{m_2 m_3 M}{m_{12} m_{23} m_{34}} \right)^{\frac{1}{2}} \\ \left(\frac{m_2 m_4}{m_{12} m_{24}} \right)^{\frac{1}{2}} & \left(\frac{m_1 m_3}{m_{14} m_{34}} \right)^{\frac{1}{2}} & \left(\frac{m_1 m_4 M}{m_{12} m_{14} m_{34}} \right)^{\frac{1}{2}} \end{pmatrix} \quad (38)$$

Of course this matrix could be expressed in terms of three Eulerian angles.

Coordinates which are symmetric with respect to the "reactants" "12" and "34" and the "products" "23" and "14" are given by Eq. (6) using the transformation matrix $\underline{R}^{\frac{1}{2}}$. For example, if all of the masses are equal

$$\underline{R}^{\frac{1}{2}} = \begin{pmatrix} 0 & 0 & -1 \\ 2^{-\frac{1}{2}} & 2^{-\frac{1}{2}} & 0 \\ -2^{-\frac{1}{2}} & 2^{-\frac{1}{2}} & 0 \end{pmatrix} \quad (39)$$

and the symmetric coordinates are²

$$Q'_1 = (m_1/4)^{\frac{1}{2}} [\underline{r}_1 + \underline{r}_2 - \underline{r}_3 - \underline{r}_4] \quad (40)$$

$$Q'_2 = (m_1/4)^{\frac{1}{2}} [-\underline{r}_1 + \underline{r}_2 - \underline{r}_3 + \underline{r}_4] \quad (41)$$

$$Q'_3 = (m_1/4)^{\frac{1}{2}} [\underline{r}_1 - \underline{r}_2 - \underline{r}_3 + \underline{r}_4] \quad (42)$$

These symmetrical coordinates for equal masses were suggested to us by E. Wigner (private correspondence). At the time, we were disturbed because we did not see how to explain them on the basis of a mobile.

The explicit formulae for the coordinates symmetric between the products and reactants for unequal masses are not given here because the sines and cosines of the Eulerian angles corresponding to \mathcal{R} and $\mathcal{R}^{\frac{1}{2}}$ are very messy when the masses are arbitrary. However, for any specific case, these symmetric coordinates would be easy to obtain.

II. THE SIGNIFICANCE OF THE SKEWED COORDINATES

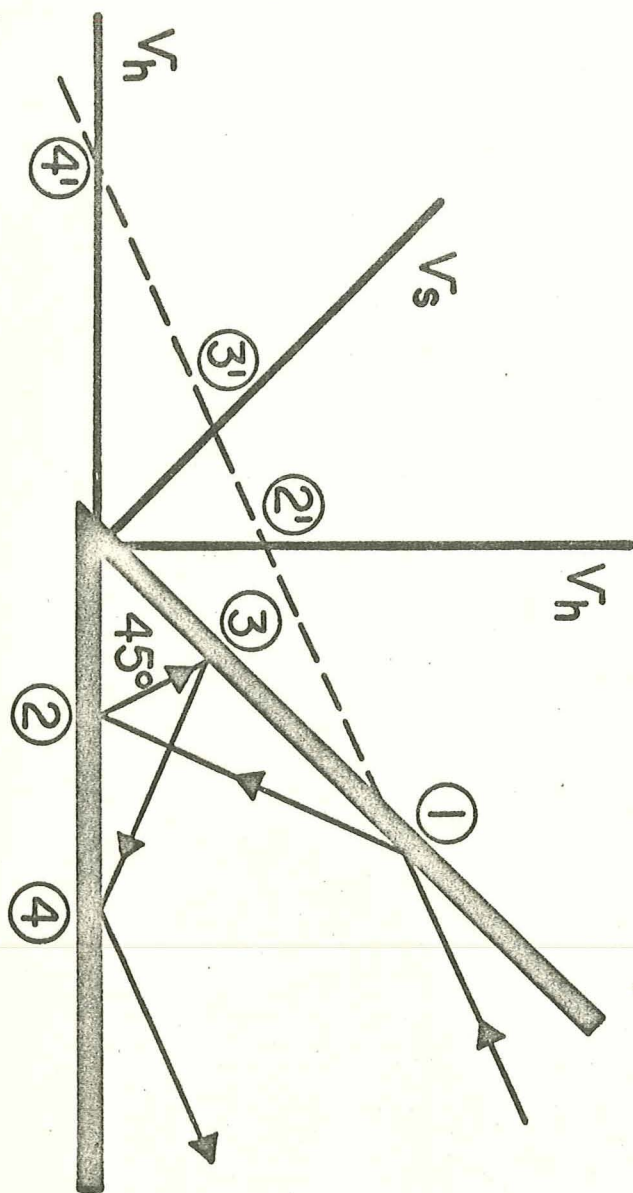
In order to get a feeling for the significance of the coordinates which diagonalize the relative kinetic energy, let us consider the motion of three rigid particles constrained to move in a line. For simplicity we assume that the potential energy is zero unless either particles "1" and "2" or "2" and "3" collide, in which case the potential energy is infinite. In Fig. 5, collisions between "1" and "2" correspond to points along the side wall; collisions between "2" and "3" correspond to points on the horizontal wall. Table 2 gives the velocities (in laboratory space) of the three particles at different points on the trajectories which are illustrated in Fig. 5. It is

Table 2: Particle Velocities (in Laboratory Space)
Corresponding to Trajectories Shown in Fig. 5.

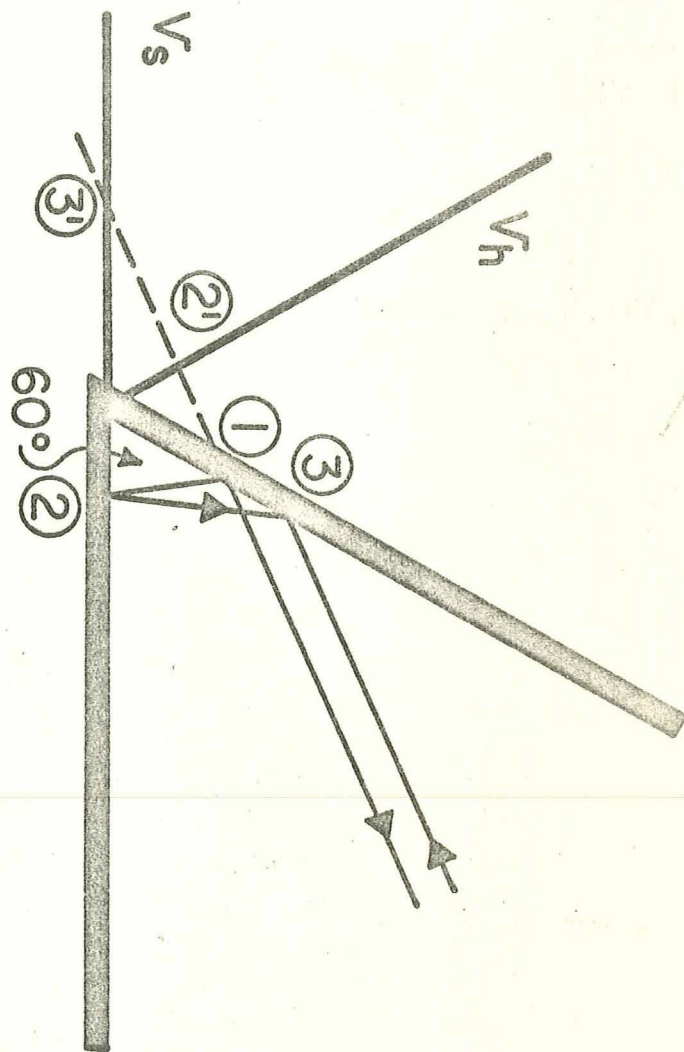
	Particle	Mass	Initial Velocity	Velocity After ①	Velocity After ②	Velocity After ③	
<u>Fig 5a</u> H-H-H	1	1	u	0	0		Exchange Reaction
	2	1	0	u	0		
	3	1	0	0	u		
<u>Fig 5b</u> T-H-D	1	3	u	u/2	u/2	0	Adiabatic Collision
	2	1	0	3u/2	-u/2	u	
	3	2	0	0	u	u	
<u>Fig 5c</u> T-H-D	1	3	0	0	-2u/3	-2u/3	Adiabatic Collision
	2	1	0	-4u/3	+2u/3	-2u/3	
	3	2	-u	-u/3	-u/3	+u/3	

convenient to think of the masses of the particles in terms of the three hydrogen isotopes H, D, and T whose relative masses are 1, 2, and 3 respectively. In the three trajectories which are illustrated, two of the particles are initially at rest. For the H-H-H system (equal masses) shown in Fig. 5a, initially we have "1" + "23", after the collision particle "2" has exchanged partners leaving "12" + "3" corresponding to an exchange reaction. If initially "2" and "3" are separated by the distance R , then after the reaction "1" and "2" are separated by the same distance. For the T-H-D system shown in Figs. 5b and 5c, the trajectories shown correspond to adiabatic collisions. The difference between the H-H-H and the T-H-D collisions is that the angle of skewing is $\phi = 60^\circ$ for the equal masses and $\phi = 45^\circ$ for the T-H-D, according to Table 1. If, now, we interchanged the positions of the H and the D to form the system T-D-H, then according to Table 1, the angle of skewing is $\phi = 63^\circ 26'$ or almost 60° . Therefore the collisions $T + DH$ or $TD + H$ would result in exchange reactions.

The trajectories on these idealized potential energy surfaces can be determined in classical mechanics by the use of the method of virtual reflections.⁷ In Fig. 6 the lines marked " v_s " are reflecting surfaces corresponding to the side wall, whereas the " v_h " are virtual images of the horizontal wall. The virtual trajectory is a straight line. Letting 0 be the origin, the triangles $(1) (2) 0$ and $(1) (2') 0$; $(2) (3) 0$ and $(2') (3') 0$; etc. are congruent. The number of turning points in the trajectory is equal to the number of intersections of the virtual trajectory with the real and virtual reflecting surfaces.



(b)



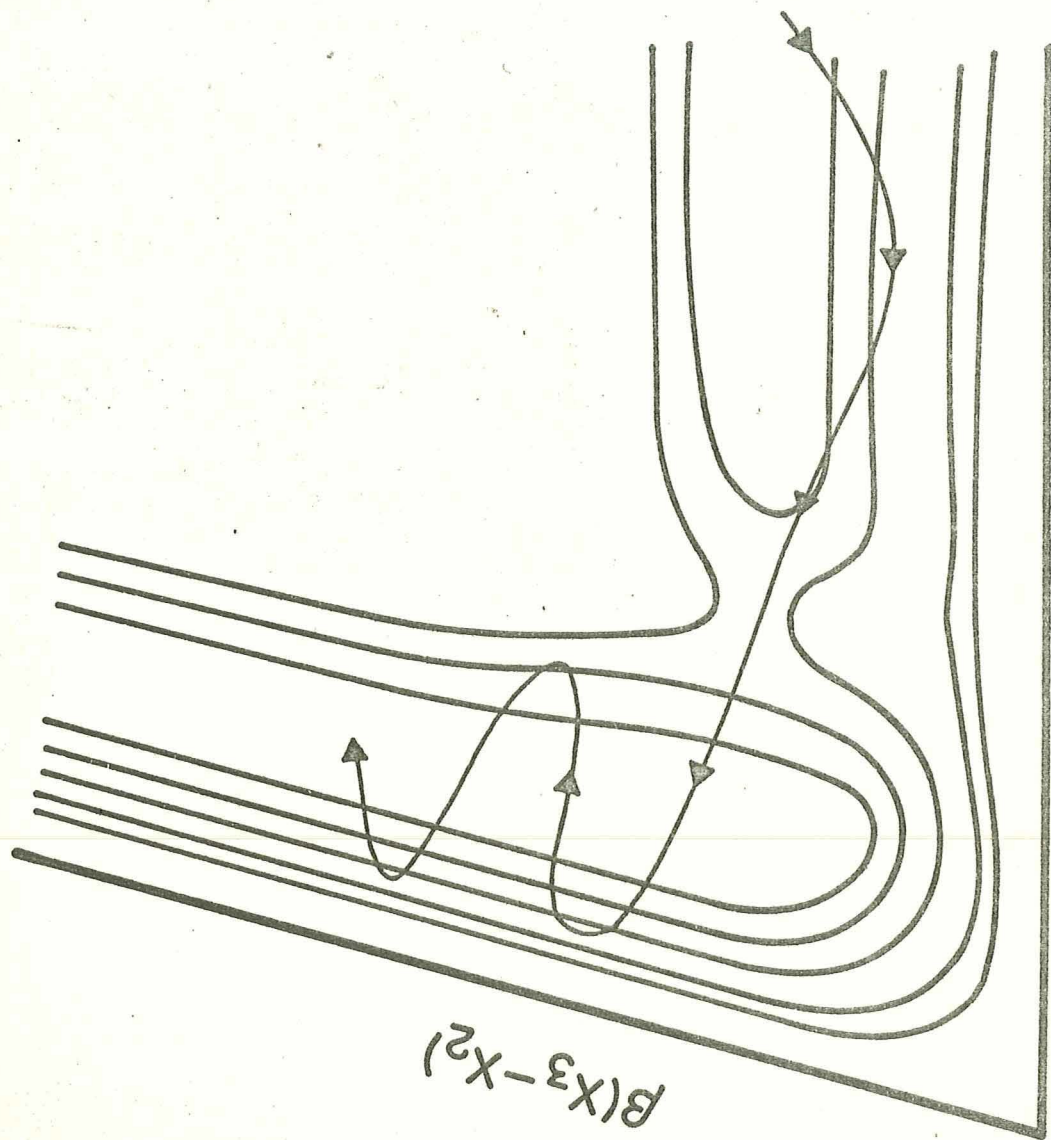
(a)

Fig. 6: General Collisions of Three Rigid Particles in a Line Showing the Use of the Method of Virtual Reflections.

Thus, the largest possible number of turning points for a trajectory on a surface with $\phi = 60^\circ$ is three (as shown in Fig. 6a); or with $\phi = 45^\circ$, it is four (as shown in Fig. 6b). Unfortunately, the method of virtual reflections does not apply in quantum mechanics as there is interference between the various segments of the trajectory. Conformal transformations cannot be used in quantum mechanics for much the same reason. Thus, the calculation of trajectories (or the corresponding wave functions) remains very difficult in quantum mechanics, even for such idealized potential energy surfaces.

In many cases, from the shape of the potential energy surface one can predict whether the energy released in a chemical reaction will take the form of vibrational or translational energy. Fig. 7 shows a schematic potential energy surface and a trajectory for a reaction $"1" + "23" \rightarrow "12" + "3"$. Because of the nature of the energy contours, almost all of the energy released in this reaction must go into the vibration of the product molecule $"12"$. Conversely, the reverse reaction could only take place if initially the molecule $"21"$ were vibrationally highly excited.

When I was a graduate student, George Kimball and Henry Eyring⁴ calculated an approximate potential energy surface for the reaction $H + Cl_2 \rightarrow HCl + Cl$ which is reproduced here as Fig. 8. To convert Fig. 8 into a proper potential energy surface, the angle between the R_{H-Cl} and the R_{Cl-Cl} should be skewed. However, for this case $\phi = 83^\circ 15'$, which is not too different from 90° . Furthermore, the horizontal scale (relative to the vertical) should be $4.25 R_{Cl-Cl}$ instead of R_{Cl-Cl} since $\beta/\alpha = 4.25$. With these changes, the



$$a(X_2 - X_1)$$

Fig. 7: Hypothetical Potential Energy Surface with Unusual Shape.

The reaction "1" + "23" \rightarrow "12" + "3" produces vibrationally excited diatomic molecules as shown by the trajectory.

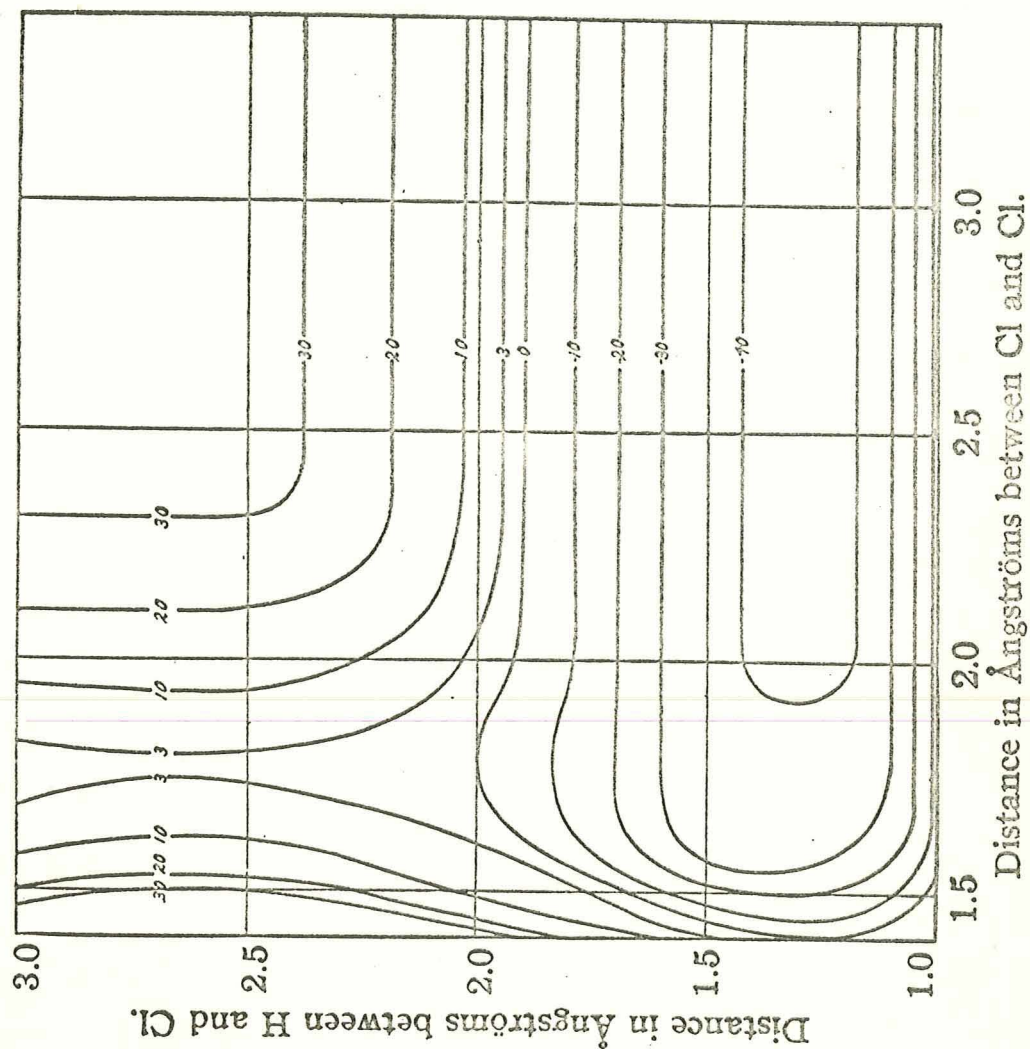


Fig. 8: Approximate Potential Energy Surface⁴ for the System H-Cl-Cl Calculated by Kimball and Eyring in 1932.

Kimball-Eyring potential energy surface would still resemble Fig. 7.

I remember that Kimball and Eyring commented that the reaction $\text{H} + \text{Cl}_2$ would lead to vibrationally excited HCl . Thus, it came as no surprise to me when John Polanyi (Michael's son) and co-workers⁵ discovered that for the reactions $\text{H} + \text{Cl}_2$ and $\text{H} + \text{Br}_2$ an appreciable fraction (approximately one-half) of the exothermal energy appeared as vibrational excitation of the products.

The construction of approximate potential energy surfaces by the crude techniques of Henry Eyring and his co-workers led to many important conclusions about reaction kinetics.⁶ Within the next few years, we can expect that very accurate potential energy surfaces will be constructed which will help to explain and predict many important features of molecular collisions and chemical kinetics.

REFERENCES

1. H. Eyring and M. Polanyi, Z. Physik. Chem. B12, 279 (1931). In this paper, the "skewed" coordinates were used for the first time. Unfortunately the angle of skewing was taken to be $(\pi - \theta)$ instead of θ . This mistake was recognized by O. K. Rice (see H. Eyring, H. Gershinowitz, and C. E. Sun, J. Chem. Phys. 3, 786 (1935)) and by J. O. Hirschfelder, Ph.D. Dissertation, Princeton University (1936).
2. D. W. Jepsen and J. O. Hirschfelder, Proc. Nat. Acad. Sci. 45, 249 (1959).
3. J. O. Hirschfelder and J. S. Dahler, Proc. Nat. Acad. Sci. 42, 363 (1956).
4. G. E. Kimball and H. Eyring, J.A.C.S. 54, 3876 (1932).
5. K. G. Anlauf, P. J. Kuntz, D. H. Maylotte, P. D. Pacey, and J. C. Polanyi, Disc. Faraday Soc. 44, 183 (1967). They used infra-red chemi-luminescence techniques. They were able to explain their experimental results on the basis of London-Eyring-Polanyi-Sato potential energy hyper-surfaces.
6. J. O. Hirschfelder, J. Chem. Phys. 9, 645 (1941) showed how to calculate quickly and easily the salient features of Eyring-type potential energy surfaces for any three or four atom system.
7. D. W. Jepsen and J. O. Hirschfelder, J. Chem. Phys. 30, 1032 (1959) developed the method of virtual reflections and considered the dynamics of three rigid particles moving in a line on idealized potential energy surfaces.